X-ray absorption spectroscopy on layered cobaltates Na_xCoO_2

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Measurements of polarization and temperature dependent soft x-ray absorption have been per-
formed on Na_xCoO_2 single crystals with x=0.4 and x=0.6. They show a deviation of the local
trigonal symmetry of the CoO_6 octahedra, which is temperature independent in a temperature
range between 25 K and 372 K. This deviation was found to be different for Co^{3+} and Co^{4+} sites.
With the help of a cluster calculation we are able to interpret the Co L_{23}–edge absorption spectrum
and find a doping dependent energy splitting between the t_{2g} and the e_g levels (10Dq) in Na_xCoO_2.

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I. INTRODUCTION

The discovery of an unexpectedly large thermopower
accompanied by low resistivity and low thermal conduc-
tivity in Na_xCoO_2 raised significant research interest in
these materials [1] and lead to a number of experimental
and theoretical investigations [2, 3, 4, 5, 6]. This interest
has strongly been reinforced by the discovery of supercon-
ductivity in the hydrated compound $Na_{0.35}CoO_2 \cdot 1.3H_2O$
in 2003 [7], and thus Na_xCoO_2 experiences an again
increasing attention [8, 9, 10, 11, 12, 13, 14, 15, 16,
17, 18, 19, 20, 21, 22, 23, 24]. The similarity of the
Na cobaltates to the high temperature superconductors
(HTSC) - both are transition metal oxides and adopt
a layered crystal structure with quasi two dimensional
$(Cu, Co)O_2$ layers - is an important aspect of the research
activities. In contrast to the HTSC cuprates however,
the CoO_2 layers consist of edge sharing CoO_6 octahedra
which are distorted in a way that the resulting symme-
try is trigonal. The trigonal coordination of the Co–sites
results in geometric frustration which favors unconven-
tional electronic ground states. The geometrically frus-
trated CoO_2–sublattice also exists in the non–hydrated
parent compound Na_xCoO_2, which has been investigated
in this work. The intercalation of water into the parent
compound is expected to have little effect on the Fermi
surface beside the increase in two–dimensionality due to
the effect of expansion [25, 26].

Upon lowering the symmetry from cubic to trigonal,
the t_{2g} states split into states with e_g^{π} and a_{1g} symmetry,
which can be represented as

$$e_{g\pm}^{\pi} = \mp \frac{1}{\sqrt{3}} [|xy\rangle + \exp^{\pm i 2\pi/3} |yz\rangle + \exp^{\pm i 4\pi/3} |xz\rangle] \quad (1)$$

and

$$a_{1g} = \frac{1}{\sqrt{3}} [|xy\rangle + |yz\rangle + |xz\rangle]. \quad (2)$$
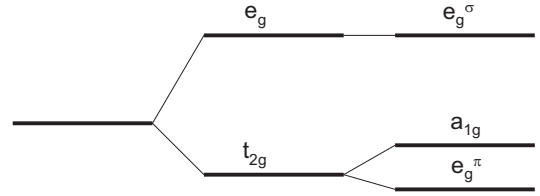
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FIG. 1: Illustration of the splitting of the energy levels for
cubic and trigonal symmetry. Here due to the trigonal distor-
tion the e_g^{π} states have been assumed to be lowest in energy.

The cubic e_g states remain degenerate and will be named
e_g^{σ} in the following in order to avoid confusion. As has
been predicted by calculations [15] and shown experimen-
tally in Ref. 16, the e_g^{π}-states are lower in energy and are
therefore filled, while the a_{1g}-states are partially filled
as a function of x. Therefore, the a_{1g}–states govern the
relevant low energy excitations.

From magnetization, specific heat, and conductivity
measurements for various doping levels, three phase tran-
sitions as a function of temperature have been observed:
a low temperature bulk antiferromagnetic transition at
$T_N \approx 20$ K for $0.75 \le x \le 0.9$ [5, 19, 20] and two high
temperature transitions at about 280 K in a $Na_{0.82}CoO_2$
sample [17] and 323–340 K in samples with $x \approx 0.75$
[27, 28]. The origin of the 280 K transition has been
discussed in terms of charge ordering and the formation
of magnetopolarons due to a charge induced Co $3d$ spin
state transition from a low spin state to an intermedi-
ate spin state [17]. Such a spin state transition occurs
for instance in the related compounds $La_{1-y}Sr_yCoO_3$
[30, 31, 32, 33]. In some samples, a third transition at
around 340 K is observed, and it was suggested that this
is due to a structural transition involving Na ordering
[27, 28, 29], which is supported by Huang *et al.* who
found a structural transition concomitant with a shift of
a large fraction of the Na ions from a high–symmetry
position to a lower–symmetry position [28].

In this article, we present measurements of the near
edge x–ray absorption fine structure (NEXAFS) of

Na_xCoO_2 (x = 0.4 and x = 0.6) which have been carried out in order to investigate the electronic properties of this interesting class of materials.

II. EXPERIMENTAL

The used single crystals were grown by two different methods. First, single crystals of $Na_{0.75}CoO_2$ were grown using the travelling solvent floating–zone method, crystals with a lower Na concentration were produced using de–intercalation with Bromium from the highly doped samples. The initial characterization of the samples has been carried out using energy dispersive x-ray analysis (EDX), x–ray diffraction and chemical analysis. Details of the crystal growth, de–intercalation, and characterization of the resulting samples will be presented elsewhere [34]. Second, high–quality single crystals were grown by the sodium chloride flux method as thoroughly described in Ref. 35. Both methods lead to the same spectra.

The NEXAFS measurements of the absorption coefficient were performed at the UE52-PGM beamline at the synchrotron facility BESSY II, Berlin, analyzing the drain current. The energy resolution was set to 0.09 eV and 0.16 eV for photon energies of 530 eV and 780 eV, respectively. We performed measurements on different non–hydrated single crystals with a sodium content of x = 0.4 and x = 0.6 at various temperatures and different polarizations of the incident synchrotron light at the oxygen K- and cobalt $L_{2,3}$–edge. The two doping levels that have been investigated belong to two different and interesting regions in the phase diagram [24], x=0.4 lies in the region of a paramagnetic metal whereas and x=0.6 is a Curie-Weiss metal. All the crystals were of the same size of about 3x3 mm^2 area and 1 mm thickness. Crystals were freshly cleaved in–situ under ultra–high vacuum conditions (about $2\cdot10^{-10}$ mbar) at 25 K, which resulted in shiny sample surfaces.

Special attention has been paid to the reproducibility of the experimental data and the effects of surface contaminations. The freshly cleaved surfaces turned out to be very sensitive to adsorbates. We observed irreversible changes in the O K–spectra when the sample surfaces were exposed to pressures above $2\cdot10^{-9}$ mbar which we attribute to adsorbed, oxygen containing molecules at the surface. No such changes have been found for the Co absorption edges. A comparison to the temperature dependent behavior of the Co $L_{2,3}$–edge proves that the origin of this irreversible effect is due to surface contamination and not due to a change or a transition of the whole sample, since the Co $L_{2,3}$–edge remains unchanged with temperature.

According to the dipole selection rules the O K and Co $L_{2,3}$ excitations as probed by these experiments, correspond to core electron transitions into unoccupied oxygen 2p and cobalt 3d electronic states. Upon variation of the incident light polarization, different O 2p and Co 3d orbitals can be probed [36]. For polarization depen-

dent measurements, the samples were oriented such that the direction of incident photons and the sample surface normal (i.e. the c–axis) enclose an angle of $\alpha = 70°$. The used undulator allows a rotation of the beam polarization by $90°$ using the vertical and horizontal mode. This procedure avoids experimental artifacts related to the differences in the optical path and the probed area. All NEXAFS results referred to E parallel to the c–axis (E||c) are corrected using the formula $I_{||c} = \frac{1}{\sin^2(\alpha)}(I - I_{\perp c}\cos^2\alpha)$ where $I_{\perp c}$ and I are measured NEXAFS intensities with $E \perp c$ and E in the plane defined by the c–axis and the incident photon beam, respectively. In order to compare the data, the NEXAFS spectra are normalized at higher energies where the absorption is doping independent and isotropic and the spectra for different measurements and settings should show the same intensities. The spectra are normalized at 600 eV for the O K–edge and at 810 eV for the Co $L_{2,3}$–edge.

III. RESULTS AND DISCUSSION

Using NEXAFS, the unoccupied energy levels close to the Fermi level can be studied by excitations from core electrons into unoccupied states. We have measured excitations from O 1s core levels into unoccupied O 2p states that are hybridized with states of primary Co and Na character, as well as excitations from Co 2p into Co 3d states. If the influence of the core hole is neglected, as is reasonable for the O 1s core hole excitations, a direct interpretation of the NEXAFS results in terms of the partial unoccupied density of states is possible, analogous to a one electron addition process [37, 38]. If the core hole cannot be neglected, as is the case for Co 3d excitations, the interpretation of the data requires consideration of multiplet splitting, hybridization and crystal field effects.

A. Co L-edge

In Fig. 2 experimental spectra of the Co $L_{2,3}$–edges are shown, which display three main features at each edge: one strong central peak (peak b and b') with a shoulder towards higher energies (peak c and c') and a peak/shoulder towards lower energies (peak a and a') (Fig. 2). This result can easily be compared to the similar compound $LiCoO_2$ which nominally contains only Co^{3+} ions with S=0 [39]. In the NEXAFS spectra of the Co $L_{2,3}$–edge of $LiCoO_2$ one finds only one main peak [40] different from the spectrum observed for the mixed valence system Na_xCoO_2. Especially the low energy feature (peak a and a') is absent in $LiCoO_2$, consequently we assign this peak to be caused by excitations into unoccupied 3d states of nominal Co^{4+} ions which are missing in $LiCoO_2$. This interpretation is furthermore supported by the doping dependence of the L–edge as the low energy peak appears stronger for lower sodium doping (i.e. higher Co^{4+} concentration) and weaker for higher sodium
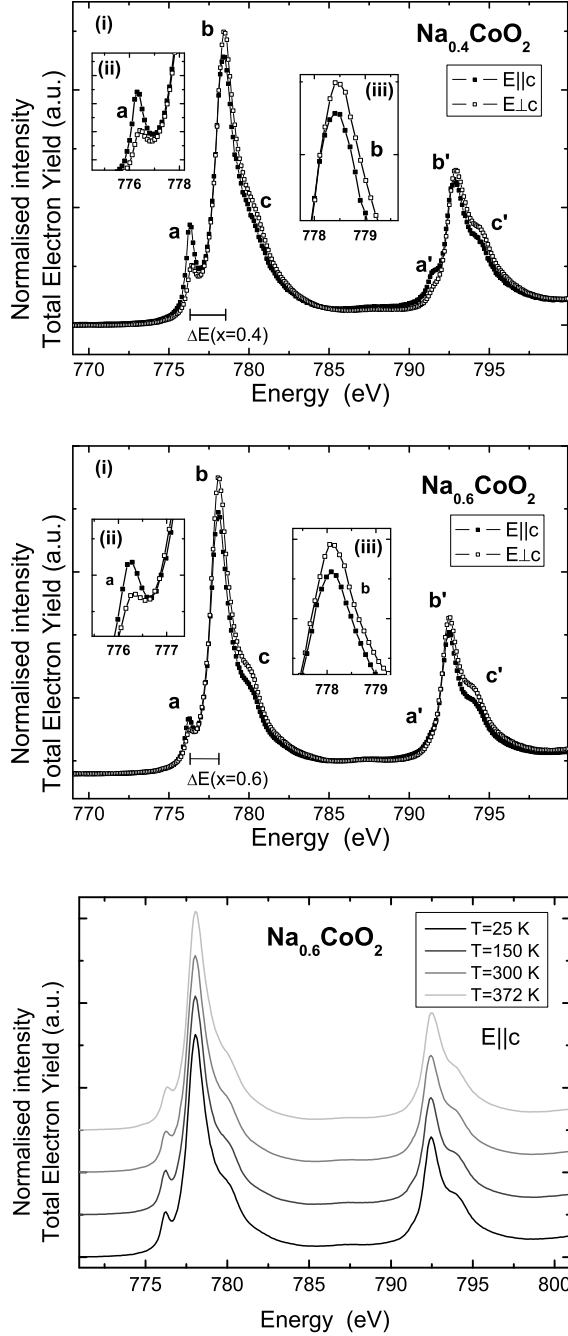
FIG. 2: Top and middle figure: Polarization dependence NEXAFS spectra of the Co $L_{2,3}$–edge for Na_xCoO_2 with x=0.4 (top) and x=0.6 (middle) at 25 K. ΔE_x represents the difference in energy between the first and the main peak. The insets show an enlargement of the region around the first peak (ii) and around the top of the main peak (iii). Bottom: No significant temperature dependence is observable between 25 and 372 K for x=0.6. All intensities are normalized at 810 eV where no stoichiometric, polarization, or temperature dependence is observable.

doping (i.e. lower Co^{4+} concentration), as well as by calculations as described below.

The local electronic structure around a Co atom in Na_xCoO_2 has been modelled in a cluster calculation using many–body wave functions. Within this approach, a CoO_6 cluster containing the Co $3d$ and the O $2p$ valence electrons has been solved exactly including all interactions between $3d$ electrons in O_h symmetry with a ground state for Co^{4+} as given in equation 2 [41]. For simplicity we will use in the following the expression Co^{4+}, referring to a (distorted) CoO_6 octahedra with a formal Co^{4+} central ion containing five holes and, analogously, Co^{3+} for an octahedra containing four holes with a formal Co^{3+} central ion. It has been found from the calculations that the first peak at lower energies in the NEXAFS Co L–edge (peak a and a' in Fig. 2) originates from excitations into Co^{4+} final states with an A_{1g} symmetry, while the main peak (b and b') and the shoulder (c and c') are due to excitations into final states of Co^{3+} with E_g symmetry and Co^{4+} with T_{1g} and T_{2g} symmetry, respectively. Note that in order to avoid confusion we labeled the final states by using capital letters (e.g. A_{1g}) while the ground is labeled with lower case letter (e.g. a_{1g}). The ground state of the system has been found to be strongly covalent with a moderate positive charge transfer energy $\Delta_{CT} = E(d^{n+1}L) - E(d^n)$ for Co^{3+} and a negative Δ_{CT} for Co^{4+} [41].

In the experimental spectrum of the Co L–edge one additionally observes that the energy difference between the first peak (A_{1g}) and the largest peak (E_g) in Fig. 2 differs between the two different stoichiometries x=0.4 and x=0.6 being $\Delta E_{x=0.4} = -2.0$ eV and $\Delta E_{x=0.6} = -1.8$ eV. Theoretically, this behavior can be best explained by a change of the energy splitting between the t_{2g} states and the e_g states (10Dq). An explanation for a lower 10Dq for higher sodium intercalation can be found from neutron powder diffraction by Huang et al. An increasing Co–O distance with increasing sodium content is found [28] which guides a lower influence of the crystal field and charge transfer, i.e. a lower 10Dq.

The a_{1g} orbital of the ground state in trigonal symmetry points along the (1 1 1) direction of the distorted CoO_6 octahedra, i.e. parallel to the crystal c–axis, while the the two e_g^π orbitals point perpendicular to it. From polarization dependent measurements with the **E** vector of photons parallel and 70° to the crystal c axis one observes the a_{1g} peak of Co^{4+} to be stronger for **E**||c as compared to **E** $\perp$ c. This behavior is expected for a local trigonal distortion, where the t_{2g} ground states split into states with a_{1g} and e_g^π symmetry, whereas the e_g^σ states remain untouched (c.f. Fig. 1) and therefore should not show a strong polarization dependence. Different from that, the intensity of the Co^{3+} central peak is significantly larger for **E** $\perp$ c compared to **E**||c (Fig. 2). This effect points to an additional distortion that splits the e_g^σ levels. Such a splitting might be caused by two mechanisms. From spectral ellipsometry on a $Na_{0.82}CoO_2$ sample, Bernhard et al. find a transition at 280 K which they
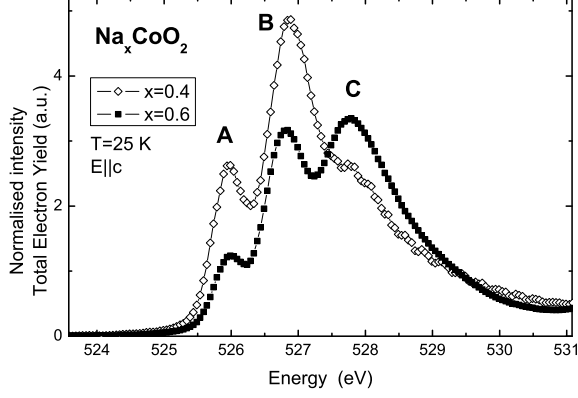
FIG. 3: Stoichiometric dependence of Na_xCoO_2 at the Oxygen K-edge. A, B, and C represent the positions of the three main peaks. The intensities are normalized at 600 eV.

explain by the formation of magnetopolarons using the idea of a spin–state transition [17] similar to the related compound $La_{1-y}Sr_yCoO_3$ [30, 31, 32, 33]. In Na_xCoO_2, this mechanism would be driven by a displacement of the neighboring oxygen ligands towards the central Co^{4+} ion which may favor an intermediate–spin (IS) state with S=1 over a low–spin (LS) state with S=0 of the Co^{3+} ions [17]. This displacement would result in a splitting of the e_g^σ levels. Another possibility for an additional distortion could arise from the effect of sodium ordering at special doping levels [28, 29, 42, 43], it is assumed that this results in orthorhombic symmetry so that a perturbation of the trigonal distortion of the octahedra could occur.

Both possible contributions are related to a corresponding ordering temperature, the formation of magnetopolarons is observed at 280 K, whereas the sodium ordering appears at temperatures below 350 K for x=0.75. However, no significant temperature dependence for $Na_{0.6}CoO_2$ has been found between 25 K and 370 K in the present NEXAFS studies. This implies that the spin–state of Co as well as the electronic structure in this energy range as seen by NEXAFS is not affected by temperature neither by a spin state transition nor by a structural transition involving Na ordering (Fig. 2 bottom). A temperature independent distortion would be expected if the non–trigonal distortion is purely structural.

B. O K-edge

In Figure 3, we present the results for the O K absorption edge of $Na_{0.4}CoO_2$ and $Na_{0.6}CoO_2$ measured with light polarized parallel to the crystallographic c axis. For both stoichiometries we observed three pronounced features A, B and C above the absorption threshold, show-
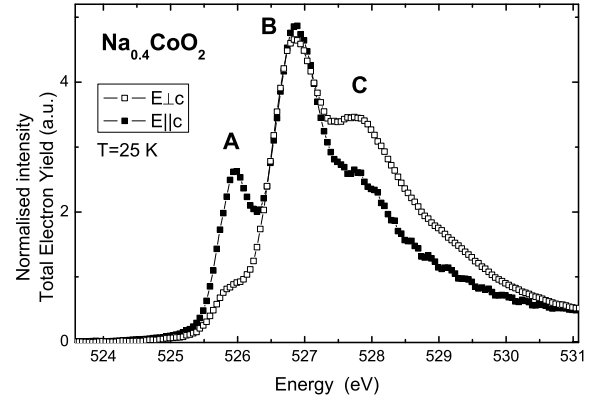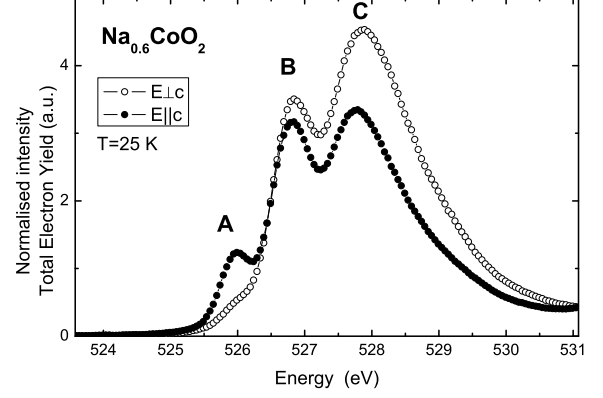

FIG. 4: NEXAFS polarization dependence of the oxygen K-edge of Na_xCoO_2 for x=0.6 (top) and x=0.4 (bottom). Polarization $E||c$ is indicated by filled symbols, $E||c$ is indicated by open symbols. The intensities are normalized at 600 eV where the spectrum is isotropic.

ing a significant doping dependence. Features A and B increase for smaller x, while feature C decreases, i.e. features A and B increase with an increasing hole doping. In the related compound $LiCoO_2$ the situation is very similar to Na_1CoO_2, since both systems are assumed to have a low–spin state meaning that all six t_{2g} states are occupied by electrons while the four e_g states are empty. The resulting absorption spectrum shows only one peak due to O $2p$ orbitals hybridized with the Co $3d$ orbitals with e_g symmetry [40]. In Na_xCoO_2, excitations into unoccupied Co^{3+} states should therefore only be responsible for a single peak in the whole O K-absorption edge spectra of Na_xCoO_2. We therefore attribute the first two features A and B in Fig. 3 to doping induced states related to the formation of Co^{4+} sites and feature C to the formation of of Co^{3+} sites, surrounded by oxygen octahedra. It has been shown previously that the pre–edge peaks in the O K NEXAFS spectra of the late transition–metal (TM)

oxides are shifted by about 1 eV to lower energies when the TM valence increases by 1 [44]; therefore, spectral features from two different valence states can be well resolved. The energetic downshift can be explained by a decrease of the energy between the partially filled Co $3d$ states; the valence electrons will be screened by 1 eV more with every added valence electron, resulting in a situation that for late transition metals a higher valency corresponds to a lower excitation energy. Upon hole addition (decreasing x), the increase of features A and B, and the decrease of feature C indicate that both are related to the doping process and it is natural to ascribe them to excitations into unoccupied O $2p$ states hybridized with Co^{3+} e_g^{σ} states (feature C) and, about 1 eV lower in energy, to excitations into unoccupied O $2p$ states hybridized with Co^{4+} e_g^{σ} states (feature B) and those hybridized with Co^{4+} a_{1g} states (feature A). Additionally, these results show that the holes in Na_xCoO_2 have a significant oxygen character, which is in good agreement with other cobalt based compounds [32, 40, 45].

Next we turn to the polarization dependence of the O K absorption edges as shown in Fig. 4. From polarization dependent absorption measurements, information about the orientation of the corresponding orbitals are obtained. Our data signal that the doping induced absorption feature A is strong for E||c, and substantially weaker for E $\perp$ c. Consequently, from the orientation of the a_{1g}–orbital and the attribution of the three peaks as described above, the holes doped into the CoO_2 layers of Na_xCoO_2 have a predominant a_{1g} character similar to the result found by Wu *et al.* using x–ray absorption spectroscopy [16]. Band structure calculations find, that although the a_{1g} and e_g^{π} states overlap, and mix to some extend, the centers of these states are energetically separated with those closer to E_F having dominant a_{1g} character [4], in good agreement with our results. In addition, while feature B is not or only slightly polarization dependent, the intensity of peak C (Co^{3+}) is significantly stronger for **E** $\perp$ c than for **E**||c. The same result has already been observed at the Co L–edge, but because of the large central peak no quantitative analysis of the polarization dependence of the Co^{4+} shoulder could be made. At the oxygen K–edge these two peaks are well separated and a difference in the response due to different polarizations is observable. From this we conclude that the trigonal symmetry is better realised in octahedra containing a Co^{4+} central ion than in octahedra containing a Co^{3+} central ion. Such a situation has already been suggested by Bernhard and coworkers as an origin of magnetopolarons [17]. As already mentioned in section III A, the underlying idea for such an effect is a lowering of the local symmetry around the Co^{3+}. Thus, the t_{2g} triplet and the e_g doublet split and become polarization dependent. The effect may be stronger at temperatures below 20 K, which is also the critical temperature for a magnetic transition to a bulk antiferromagnetic ordered state [20, 24], at temperatures lower than 20 K the mobility of the magnetopolarons is assumed to be lower due
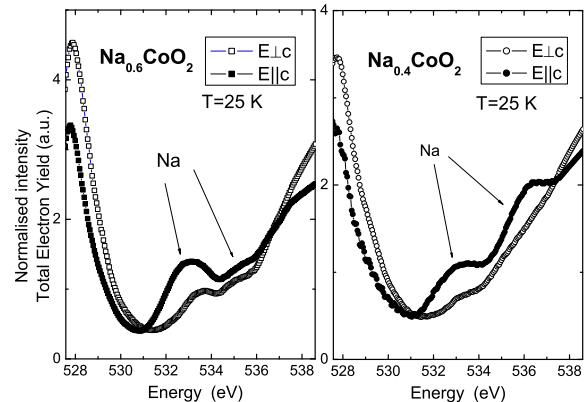

FIG. 5: Stoichiometric and polarization dependence of the NEXAFS spectra of Na_xCoO_2 at the oxygen K–edge. The energy range right above the oxygen threshold is shown where the the hybridization between O and Na can be monitored. All curves are normalized at 600 eV.

to an increased self–trapping energy in the antiferromagnetic state [17].

Somewhat higher in energy at E $\approx$ 535 eV, one finds the excitations into unoccupied O levels which are hybridized with Na orbitals [16]. As expected, the resulting peaks increase in intensity with increasing sodium intercalation, but in addition they are strongly polarization dependent. As is shown in Fig. 5 the intensity for $\vec{E}||c$ is stronger than for $\vec{E} \perp c$. This leads to a finite Na–O hybridization along c, a consequence of this hybrid could be a 3 dimensional magnetism as has been proposed by Johannes *et al.* [46]. From our data it becomes clear, that the inter–planar binding is more likely to have a covalent rather than an ionic character, so that a 3D magnetism is reasonable.

IV. CONCLUSION AND SUMMARY

The study of single crystals with a stoichiometry $Na_{0.4}CoO_2$ and $Na_{0.6}CoO_2$ reveal polarization dependencies that cannot be explained by a simple trigonal distortion of the CoO_6 octahedra. Taking the results of both, the Co $L_{2,3}$–edge and the O K–edge into account, it follows that an additional distortion is present which is stronger for octahedra with a formal Co^{3+} central ion than for octahedra with a formal Co^{4+} central ion. A possible explanation for such a phenomena has been given by Bernhard *et al.* who find magnetopolarons in $Na_{0.82}CoO_2$ due to a lowering of the local symmetry [17]. Furthermore, we find doping dependent relative peak positions at the Co $L_{2,3}$–edge which can be explained by a doping dependent splitting of the t_{2g}–e_g levels (10Dq) as has been found from cluster calculations and can be

explained by a doping dependent Co–O bond distance [28]. At the O K–edge we find excitations into unoccupied O levels which are hybridized with Na orbitals to be strongly polarization dependent, which emphasizes the covalent character of the inter–planar binding of the CoO_2 and Na planes, rather than an ionic character.

Acknowledgment

[1] I. Terasaki, Y. Sasago, and K. Uchinokura, Phys. Rev. B **56** R12685 (1997)

[2] R. Ray, A. Ghoshray, and K. Ghoshray, and S. Nakamura, Phys. Rev. B **59** 9454 (1999)

[3] W. Koshibae, K. Tsutsui, and S. Maekawa, Phys. Rev. B **62** 6869 (2000)

[4] D.J. Singh, Phys. Rev. B **61** 13397 (2000)

[5] T. Motohashi, R. Ueda, E. Naujalis, T. Tojo, I. Terasaki, T. Atake, M. Karppinen, and H. Yamauchi, Phys. Rev. B **67** 064406 (2003)

[6] Y. Wang, N.S. Rogado, R.J. Cava, and N. P. Ong, Nature **423** 425 (2003)

[7] K. Takada, H. Sakurai, E. Takayama-Muromachi, F. Izumi, R.A. Dilanian, and T. Sasaki, Nature **422** 53 (2003)

[8] B. Lorenz, J. Cmaidalka, R.L. Meng, and C.W. Chu, Phys. Rev. B **68** 132504 (2003)

[9] J.D. Jorgensen, M. Avdeev, D.G. Hinks, J.C. Burley, and S. Short, Phys. Rev. B **68** 214517 (2003)

[10] G. Baskaran, Phys. Rev. Lett. **91** 097003 (2003)

[11] D.J. Singh, Phys. Rev. B **68** 20503 (2003)

[12] D.P. Chen, H.C. Chen, A. Maljuk, A. Kulakov, H. Zhang, P. Lemmens, and C. T. Lin, Phys. Rev. B **70** 024506 (2004)

[13] S.Y. Li, L. Taillefer, D.G. Hawthorn, M.A. Tanatar, J. Paglione, M. Sutherland, R.W. Hill, C.H.Wang, and X.H. Chen, Phys. Rev. Lett. **93** 056401 (2004)

[14] A. Chainani, T. Yokoya, Y. Takata, K. Tamasaku, M. Taguchi, T. Shimojima, N. Kamakura, K. Horiba, S. Tsuda, S. Shin, D. Miwa, Y. Nishino, T. Ishikawa, M. Yabashi, K. Kobayashi, H. Namatame, M. Taniguchi, K. Takada, T. Sasaki, H. Sakurai, and E. Takayama-Muromachi, Phys. Rev. B **69** 180508 (2004)

[15] W. Koshibae and S. Maekawa, Phys. Rev. Lett. **91** 257003 (2003)

[16] W.B. Wu, D. J. Huang, J. Okamoto, A. Tanaka, H.J. Lin, F.C. Chou, A. Fujimori, and C.T. Chen, Phys. Rev. Lett. **94** 146402 (2005)

[17] C. Bernhard, A.V. Boris, N.N. Kovaleva, G. Khaliullin, A.V. Pimenov, Li Yu, D.P. Chen, C.T. Lin, and B. Keimer, Phys. Rev. Lett. **93** 167003 (2004)

[18] M. Kubota, K. Takada, T. Sasaki, H. Kumigashira, J. Okabayashi, M. Oshima, M. Suzuki, N. Kawamura, M. Takagaki, and K. Ono, Phys. Rev. B **70** 12508 (2004)

[19] M. Mikami, M. Yoshimura, Y. Mori, Takatomo Sasaki, R. Funahashi, and Masahiro Shikano, Jpn. J. Appl. Phys. **42** 73837386 (2003)

[20] S.P. Bayrakci, C. Bernhard, D.P. Chen, B. Keimer, R.K. Kremer, P. Lemmens, C.T. Lin, C. Niedermayer, and J. Strempfer, Phys. Rev. B **69** 100410 (2004)

[21] A.T. Boothroyd, R. Coldea, D.A. Tennant, D. Prabhakaran, L.M. Helme, and C.D. Frost, Phys. Rev. Lett. **92** 197201 (2004)

[22] M. Indergand, Y. Yamashita, H. Kusunose, and M. Sigrist, Phys. Rev. B **71** 214414 (2005)

[23] T. Mizokawa, L.H. Tjeng, H.-J. Lin, C.T. Chen, R. Kitawaki, I. Terasaki, S. Lambert, and C. Michel, Phys. Rev. B **71** 193107 (2005)

[24] M.L. Foo, Y. Wang, S. Watauchi, H.W. Zandbergen, T. He, R.J. Cava, and N.P. Ong, Phys. Rev. Lett. **92** 247001

[25] M.D. Johannes and D.J. Singh, Phys. Rev. B **70** 014507 (2004)

[26] H. Rosner, S.-L. Drechsler, G. Fuchs, A. Handstein, A. Wälte, K.-H. Müller, Braz. Jour. Phys. **33** 718 (2003)

[27] B.C. Sales R. Jin, K.A. Affholter, P. Khalifah, G.M. Veith, and D. Mandrus, Phys. Rev. B **70** 174419 (2004)

[28] Q. Huang, B. Khaykovich, F.C. Chou, J.H. Cho, J.W. Lynn, and Y. S. Lee, Phys. Rev. B **70** 134115 (2004)

[29] J. Geck, M. v. Zimmermann, H. Berger, S.V. Borisenko, H. Eschrick, K. Koepernik, M. Knupfer, and B. Büchner, cond-mat/0511554 (2005)

[30] O. Toulemonde, N. N.Guyen, F. Studer, and A. Traverse, Jour. of Solid State Chem. **158** 208-217 (2001)

[31] C. Zobel, M. Kriener, D. Bruns, J. Baier, M. Grüninger, T. Lorenz, P. Reutler, and A. Revcolevschi, Phys. Rev. B **66** 020402 (2002)

[32] S. Yamaguchi, Y. Okimoto, H. Taniguchi, and Y. Tokura, Phys. Rev. B **53** 2926 (1996); **55** 8666 (1997)

[33] N.N. Loshkareva, E.A. Ganshina, B.I. Belevtsev, Y.P. Sukhorukov, E.V. Mostovshchikova, A.N. Vinogradov, V.B. Krasovitsky, and I. N. Chukanova, Phys. Rev. B **68** 024413 (2003)

[34] C. Sekar, G. Krabbes *et al.* to be published

[35] M.N. Iliev, A.P. Litvinchuk, R.L. Meng, Y.Y. Sun, J. Cmaidalka, and C.W. Chu, Physica C **402** 239 (2004)

[36] J. Fink, N. Nücker, E. Pellegrin, H. Romberg, M. Alexander, and M. Knupfer, J. Electron Spectosc. Relat. Phenom. **66** 395 (1994)

[37] F.M.F. de Groot *et al.*, Phys. Rev. B **40** 5715 (1989)

[38] F.M.F. de Groot, Coor. Chem. Rev., **249** 31 (2005)

[39] W.D. Johnston, R.R. Heikes and D. Sestrich, J. Phys. Chem. Solids, **7** 1 (1958)

[40] J. van Elp, J.L. Wieland, H. Eskes, P. Kuiper, G.A. Sawatzky, F.M.F. de Groot, and T.S. Turner, Phys. Rev. B **44** 6090 (1991)

[41] T. Kroll, A.A. Aligia, and G.A. Sawatzky, in preparation

[42] H.W. Zandbergen, M. Foo, Q. Xu, V. Kumar, and R.J. Cava, Phys. Rev. B **70** 024101 (2004)

[43] P. Zhang, R.B. Capaz, M.L. Cohen, and S.G. Louie, Phys. Rev. B **71** 153102 (2005)

[44] Z. Hu, G. Kaindl, S.A. Warda, D. Reinen, F.M.F. de Groot, and B.G. Muller, Chemical Physics **232** 63-74 (1998)

[45] Z. Hu, Hua Wu, M.W. Haverkort, H.H. Hsieh, H.J. Lin, T. Lorenz, J. Baier, A. Reichl, I. Bonn, C. Felser, A. Tanaka, C.T. Chen, and L.H. Tjeng, Phys. Rev. Lett. **92** 207402 (2004)

[46] M.D. Johannes, I.I. Mazin, and D.J. Singh, Phys. Rev. B **71** 214410 (2005) (2004)